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Sorption of 2,3,7,8-Tetrachlorodibenzo-p-dioxin to Soils from Water/Methanol Mixtures

Maryland Univ., College Park

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16. ABSTRACT

Sorption of ^{14}C-labeled 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) to soils from water/methanol mixtures has been evaluated by batch shake testing. Uncontaminated soils from Times Beach, MO, were used in these experiments and ranged in fraction organic carbon (f_{OC}) from 0.0066 to 0.077. Volume fraction methanol in the liquid phase (f_S) was varied between 0.25 and 1.0. Contact times ranging from 1 to 90 days were employed. Sorption kinetics were influenced by soil type and f_S; at f_S of 0.5, sorption equilibrium for low-f_{OC} soils was achieved within 1 day, while sorption to the high-f_{OC} soil required as long as 30 days to reach equilibrium. For f_S of 1.0 and the high-f_{OC} soil, sorption equilibrium was attained in about 10 days. Sorption isotherms were linear, and when sorption partition coefficients (K_D, mL/g) were converted to K_m (mol/g), these latter values were log-linearly related to f_S. K_m values for two soils, when normalized on f_{OC}, gave values of $K_{m,OC}$ that collapsed onto a single line having the equation determined by linear regression analysis: $\log K_{m,OC} = -4.97 f_S + 5.30$ with $r^2 = 0.98$ and $s = 0.20$. $\log K_{OC}$, the logarithm of the aqueous-phase partition coefficient normalized on f_{OC}, for TCDD extrapolated from this relationship is 6.6 + 0.7. The slope of the log-linear relationship is related to the effect of f_S on TCDD solubility and on TCDD-soil and solvent-soil interactions. Data presented here suggest that the latter solvent-soil interactions may not increase TCDD accessibility to soil organic matter to the same extent as that reported for less hydrophobic organic solutes.

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Sorption of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin to Soils from Water/Methanol Mixtures

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■ Sorption of ^{14}C-labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) to soils from water/methanol mixtures has been evaluated by batch shake testing. Uncontaminated soils from Times Beach, MO, were used in these experiments and ranged in fraction organic carbon (f_{oc}) from 0.0066 to 0.077. Volume fraction methanol in the liquid phase (f_s) was varied between 0.25 and 1.0. Contact times ranging from 1 to 90 days were employed. Sorption kinetics were influenced by soil type and f_s; at f_s of 0.5, sorption equilibrium for low-f_{oc} soils was achieved within 1 day, while sorption to the high-f_{oc} soil required as long as 30 days to reach equilibrium. For f_s of 1.0 and the high-f_{oc} soil, sorption equilibrium was attained in about 10 days. Sorption isotherms were linear, and when sorption partition coefficients (K_D, mL/g) were converted to K_m (mol/g), these latter values were log-linearly related to f_s. K_m values for two soils, when normalized on f_{oc}, gave values of $K_{m,oc}$ that collapsed onto a single line having the equation determined by linear regression analysis: $\log K_{m,oc} = -4.97 f_s + 5.30$ with $r^2 = 0.98$ and $s = 0.20$. $\log K_{oc}$, the logarithm of the aqueous-phase partition coefficient normalized on f_{oc}, for TCDD extrapolated from this relationship is 6.6 ± 0.7. The slope of the log-linear relationship is related to the effect of f_s on TCDD solubility and on TCDD–soil and solvent–soil interactions. Data presented here suggest that the latter solvent–soil interactions may not increase TCDD accessibility to soil organic matter to the same extent as that reported for less hydrophobic organic solutes.

Introduction

The compound 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is one of the most toxic compounds known to man. Experimental studies of the toxicity of TCDD with guinea pigs indicate that the LD_{50} is as low as 0.6–2.0 μg/kg of body weight (*1*).

TCDD has perhaps received the most widespread national attention because it was present in waste oils that were used for dust control in Missouri. Soil samples in the Times Beach, MO, area have been found to contain TCDD at levels as high as 1600 ng/g (*2*).

On the basis of the low reported water solubility [S, as low as 12.5 ng/L (*3*)] and high octanol–water partition coefficient [K_{ow}, $\log K_{ow} = 6.64$ (*4*)] of TCDD, this compound is expected to be immobile with respect to movement through soils by groundwater leaching. Experiments to evaluate dioxin transport in water through soils have confirmed the low mobility of TCDD (*5*) and 1,3,6,8-TCDD (*6*). However, field observations (*7*) have suggested that TCDD and other dioxins move more rapidly through soils than would be predicted on the basis of either S or K_{ow}. This "facilitated transport" has been explained in terms of numerous potential factors including enhanced solubility due to the presence of organic cosolvents in the liquid phase (*8–10*).

This study was conducted to evaluate the effect of the presence of methanol, a model miscible solvent, on the sorption of TCDD to soils and to evaluate the applicability of the cosolvent theory (*8*) to the sorption of TCDD. Methanol was selected because of its heavy industrial use and frequency of disposal at landfills and to enable direct comparison of this work to previous work utilizing methanol to evaluate the sorptive behavior of other organic solutes in the presence of cosolvents (*9*, *10*).

Theory

The cosolvent theory proposed to describe sorption of hydrophobic organic compounds to soils from water/miscible solvent mixtures (*8*) has been applied to the sorption of several organic compounds of moderate and intermediate hydrophobicity (*9*, *10*). The theory predicts a log–linear relationship between the mole-based equilibrium sorption partition coefficient (K_m) and volume fraction solvent (f_s). In its simplest form, the theory can be expressed as

$$\log (K_{m,i}/K_{m,w}) = -\alpha\sigma f_s \qquad (1)$$

where $K_{m,i}$ and $K_{m,w}$ are mole-based partition coefficients (mol/g) for water/solvent mixture i and solvent-free water, respectively. Values of $K_{m,i}$ for liquid phase i are determined from the linear sorption isotherm equation:

$$q_e = K_{D,i} C_e \qquad (2)$$

where $K_{D,i}$ is the volume-based sorption partition coefficient (mL/g) corresponding to liquid phase i, C_e is the equilibrium concentration of solute in the liquid phase (μg/mL), and q_e is the equilibrium concentration of solute in the soil phase (μg/g). $K_{m,i}$ and $K_{D,i}$ are related by

$$K_{m,i} = K_{D,i}/V_i \qquad (3)$$

where V_i is the molar volume of the liquid phase (mL/mol). The σ_s term in eq 1 reflects solute–liquid interactions in that it is the slope of the log–linear relationship between mole fraction solubility and f_s (*11*). The α term in eq 1 is related to solute–soil and solvent–soil interactions via liquid and organic carbon phase activity coefficients (*8*, *10*).

The cosolvent theory is important for two reasons. First, the theory enables prediction of sorption of an organic solute from a specified mixture of water and miscible organic solvent. This has implications on understanding fate and transport of organic contaminants in real-world, complex waste streams such as industrial wastes and landfill leachates. Second, the theory can be utilized to estimate K_D for sorption from aqueous solution by log–linear extrapolation of $K_{D,i}$ data generated at higher f_s. This is particularly significant for highly hydrophobic compounds such as TCDD because direct experimental determinations of sorption from water are extremely difficult to make.

Experimental Section

Details of the experimental protocols employed in this investigation are presented by Guiseppi-Elie (*12*) and are reviewed below.

Materials. Radiolabeled [^{14}C]TCDD was obtained from Cambridge Isotope Laboratories (Cambridge, MA) with specific activity of 33.24 mCi/mmol. TCDD had a radio-

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Table I. Soil Identification and Characterization Data

soil no.	91	92	93	94	95	96
sampling location	Sontag Road	Bubbling Springs	Times Beach	Times Beach	Shenandoah Stable	Piazza Road
site no.	04114B	03139B	06107	06109	01153B	06126B
pH[a]	6.8	5.7	7.1	7.1	7.5	5.8
CEC, mequiv/100 g[a]	5.4	10.3	10.8	10.6	16.7	15.3
organic carbon, %[b]	0.62, 0.69	0.97, 0.83	1.32, 1.35	1.57, 1.60	3.44, 2.83	7.65, 6.6, 8.9
organic nitrogen, %[b]	0.07	0.14	0.14	0.16	0.27	0.28
organic matter, %[a]	0.9	1.2, 1.4	2.0	2.3	5.0	6.3, 6.4
texture[a]						
% sand	44	24	24	22	42	38
% silt	42	56	52	56	30	40
% clay	14	20	24	22	28	22

[a] Determined by the University of Maryland Soils Testing Laboratory according to techniques described by Means et al. (*13*). [b] Determined with a Model PE-240B elemental analyzer at the Chesapeake Biological Laboratory, Solomons, MD.

chemical purity exceeding 99% and was used as received without further purification. Capillary gas chromatography/electron capture detection (GC/ECD) analyses confirmed no significant levels of other dioxin congeners in the [^{14}C]TCDD. Methanol was of pesticide grade from Fisher. Water was demineralized and organic-free and was generated by using a Hydro (Chapel Hill, NC) system employing reverse osmosis, mixed bed ion exchange, and activated carbon cartridges. Water was adjusted to an ionic strength of 0.01 M with $CaCl_2$ and was dosed with sodium azide (0.01% by weight) to inhibit microbial activity. Instagel cocktail was obtained from Packard.

Soils. Six soils, including soils collected from Times Beach, MO, were used in these studies. U.S. Environmental Protection Agency (EPA) location and site identification numbers for these soils are shown in Table I. Soils were air dried and sieved through 0.3-mm standard sieves. Sieved soils were characterized by the University of Maryland Soils Testing Laboratory for pH, cation exchange capacity (CEC), organic matter content, and texture according to methods described by Means et al. (*13*). Organic carbon and nitrogen content were determined by using a Model 240B Perkin-Elmer elemental analyzer. Organic carbon and organic matter data for soils 91–95 were in consistent agreement; the ratio of organic carbon to organic matter ranged from 0.63 to 0.73 with an average of 0.68 and standard deviation of 0.04. The data for soil 96 gave an anomalous ratio, despite consistency among replicate analyses. The average f_{oc} of soil 96 based on direct measurement was 0.077, as compared to a value of 0.043 estimated from organic matter data for soil 96 and the average ratio of organic carbon to organic matter observed for soils 91–95. The former value has been used in all subsequent calculations involving f_{oc}. Soil numbers ranging from 91 to 96 were assigned according to organic matter content to aid in computer transmittal of data to the EPA.

Batch Shake Testing. Batch shake testing was used to generate kinetic and equilibrium sorption isotherm data. Experiments were conducted in 15-mL glass conical centrifuge tubes fitted with both Teflon and aluminum foil lined screw caps. Four f_s values (0.25, 0.5, 0.75, and 1.0) and five contact periods (1, 3, 10, 30, and 90 days) were utilized. TCDD was added to the tubes either by direct injection of a solution of TCDD in methanol or by precoating in which the TCDD/methanol solution was dosed to the tube and methanol evaporated into nitrogen. TCDD doses ranged from 0.02 to 0.4 μg/tube. Soil (50 or 300 mg) and 12 mL of the liquid phase were added to the tubes, and the tubes were sealed and placed on a shaking table for contacting. The relative quantities of soil, liquid, and TCDD were generally selected to result in 20–80% of total TCDD added to each tube being sorbed to minimize experimental uncertainty (*14*). TCDD doses were selected so as to result in liquid-phase concentrations ranging from analytical detection limits (0.1 μg/L) to the estimated upper limit (0.5 S) below which sorption isotherms were expected to be linear (*15*).

Each isotherm determination consisted of 16 tubes; triplicate tubes for each of five TCDD doses and one blank tube containing soil and no TCDD. Hence, each isotherm consisted of 15 individual points. For contacting, tubes were placed horizontally on a shaking table, and mixing was provided at low speed for 2 min at 30-min intervals over the initial day of each isotherm. After the first day of contacting, tubes were removed from the shaking table and were subsequently agitated daily by manual shaking. This practice was employed to minimize colloidal particle formation, which was visually observed as an increase in liquid-phase turbidity under continuous, rigorous agitation. Following the contact period, tubes were centrifuged for 6 min at 3000 rpm (800g), and three 1-mL aliquots of centrifuged liquid phase were carefully withdrawn from the upper region of the centrifuge tubes for liquid scintillation counting (LSC). Liquid-phase TCDD concentrations were determined from the LSC results following quench and fluorescence correction. Soil TCDD concentrations were determined from the difference between initial TCDD dose and total TCDD in the liquid phase.

These experimental procedures were rigorously evaluated, particularly with regard to (1) confirmation of TCDD mass balances, (2) the effect of precoating versus direct dosing on observed K_D, and (3) effectiveness of the centrifugation procedure. The results of these studies are reported by Guiseppi-Elie (*12*) and indicate no significant experimental bias was contributed by these factors.

Liquid Scintillation Counting. Liquid samples of 1-mL volume were added to 10-mL of Instagel scintillation cocktail and counted by using a Packard Model 4000 LSC. Automatic quench correction with an external standard and fluorescence correction were employed on all samples.

Isotherm Data Analysis. Isotherm data were evaluated by linear regression to determine best fit parameters for eq 2 and statistical parameters according to techniques presented by Gillingham and Hein (*16*) and McCuen (*17*). Isotherm data were also evaluated by using a linear equation with intercept (i.e., $q_e = K_D C_e + b$) and the Freundlich equation (i.e., $q_e = K_F C_e^{1/n}$). However, these results indicated that isotherms were all linear ($1/n$ approximately 1) and that the intercept b was essentially zero. Hence, these coefficients are not reported here.

Results and Discussion

Results of linear regression analyses of sorption isotherm data for f_s of 0.5 and 1.0 are summarized in Tables II and III, respectively. Information in Tables II and III includes

Table II. Summary of Isotherm Results for Sorption of TCDD at f_s = 0.5

soil	parameter	contact time, days: 1	1	3	3[a]	10	30	30[a]	90
91	K_D	110	110	120	100	160	120		91
	n	9	9	9	12	12	9		10
	r^2	0.97	0.94	0.99	0.98	0.93	0.99		0.98
	s	0.07	0.11	0.04	0.04	0.21	0.04		0.07
92	K_D	110		94	88		96		160
	n	12		11	15		15		8
	r^2	0.97		0.80	0.98		0.99		0.65
	s	0.10		0.32	0.06		0.04		0.35
93	K_D	50		450	110		210	270	100
	n	15		6	15		8	15	14
	r^2	0.97		0.99	0.96		0.62	0.99	0.23
	s	0.10		0.05	0.11		0.55	0.06	1.7
94	K_D	49		510	110		230	250	100
	n	15		6	15		5	14	14
	r^2	0.98		0.98	0.98		0.70	0.94	0.87
	s	0.09		0.08	0.07		0.33	0.13	0.42
95	K_D	160		200	140	120	340	110	180
	n	12		14	15	9	9	13	9
	r^2	0.95		0.77	0.99	0.30	0.87	0.99	0.98
	s	0.17		0.94	0.04	0.77	0.32	0.02	0.06
96	K_D	410	410	560	630	800	1400		1500
	n	15	15	15	15	15	15		14
	r^2	0.98	0.97	0.91	0.97	0.95	0.99		0.99
	s	0.30	0.47	0.72	0.11	0.61	0.26		0.33

[a] These replicate isotherm determinations employed 300 mg of soil rather than 50 mg of soil to improve statistics. Tabulated values include K_D ($K_D = \sum C_e q_e / \sum C_e^2$), the number of isotherm points n, the coefficient of determination ($r^2 = K_D \sum C_e q_e / \sum q_e^2$), and the standard error of the estimate ($s = [(\sum (q_e - K_D C_e)^2)/(n-1)]^{1/2}$) as presented by Gillingham and Hein (*16*) and McCuen (*17*).

Table III. Summary of Isotherm Results for Sorption of TCDD at f_s = 1.0

soil	parameter	contact time, days[a]: 1	1	3	10	30	90
91	K_D	0.35	0.48	0.57	1.0		
	n	9	11	9	11		
	r^2	0.56	0.69	0.33	0.63		
	s	0.004	0.003	0.007	0.011		
96	K_D	7.6	7.9	8.9	10	11	11
	n	15	15	15	15	15	11
	r_2	0.98	0.99	0.94	0.97	0.99	0.95
	s	1.2	0.008	0.029	0.022	0.017	0.029

[a] See Table II footnote.

K_D, the number of sorption data points used in the regression analysis (n), the coefficient of determination (r^2), and the standard error of the estimate (s).

An assessment of uncertainty in calculated values of C_e, q_e, and K_D by propagation of errors indicated that the uncertainties in these values were generally ±3, ±10, and ±15%, respectively. Comparison of results from replicate tubes within a given isotherm and of replicate isotherms (see Table II, soils 91 and 96, 1-day contact) showed agreement with these uncertainties, suggesting that nonrandom errors were minimal in these experiments.

Sorption Kinetics. K_D values presented in Table II for a f_s of 0.5 for soils 91 and 96 are plotted in Figure 1. These data show that sorption equilibrium for soil 91 is attained in 1 day or less. This rapid approach to equilibrium was also observed for sorption of TCDD to soils 92–95 and for sorption from methanol. In contrast, at a f_s of 0.5, significantly longer contact times were required to attain sorption equilibrium for soil 96. The curve representing the data for soil 96 in Figure 1 is based on an equilibrium K_D (K_D^*) of 1450 mL/g and on an exponential (first-order) rate constant of 0.11 day^{-1} determined by linear regression of ln $[(K_D^* - K_D)/K_D^*]$ versus time. It is unclear why sorption to soil 96 attains equilibrium slowly, though it is suspected that the relatively slow

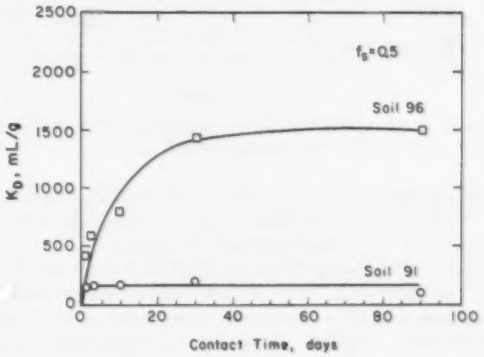

Figure 1. Kinetic data for sorption of TCDD to soils 91 and 96 at f_s = 0.5.

sorption kinetics may be attributed to differences in the organic matter content of soil 96 relative to that of the other soils.

Isotherm Linearity. It was anticipated that sorption isotherms would be linear (i.e., described by eq 2) for data corresponding to C_e values up to half of solute solubility (S) in the liquid phase (*15*). Hence, experiments were designed to yield C_e values below 0.5 S, where S for a given f_s was estimated by log–linear interpolation (*11*) with values of S for water and methanol of 0.2 μg/L (*1*) and 10 mg/L (*1*), respectively. However, the data of some isotherms for which C_e values were expected to be in a linear region of the isotherm on this basis appeared to suggest nonlinear isotherm behavior, with Freundlich exponents ($1/n$) of up to 1.5 (*12*).

To better define isotherm linearity limits, an isotherm experiment was prepared so as to span an extended range in C_e. The results of this experiment are plotted in Figure 2 and show an isotherm linearity limit for a f_s of 0.5 to be about 0.003–0.008 μg/mL rather than at 0.02 μg/mL as was originally anticipated. This modified linearity limit agrees with the log–linear estimate of 0.5S of 0.005–0.007

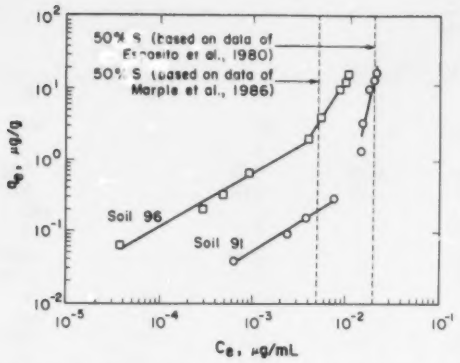

Figure 2. Extended range isotherms for sorption of TCDD to soils 91 and 96 at $f_s = 0.5$.

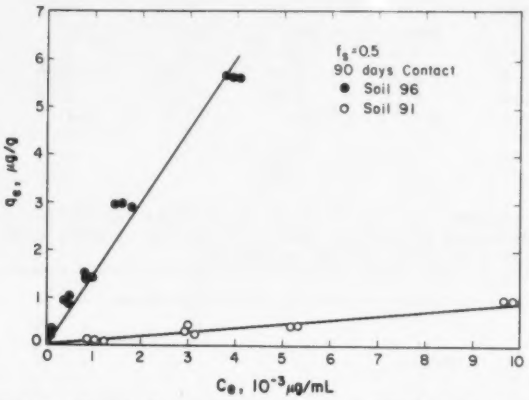

Figure 3. Linear isotherm plots for sorption of TCDD to soils 91 and 96 at $f_s = 0.5$ and 90-day contact period.

μg/mL determined on the basis of the water solubility data for TCDD reported by Marple et al. (*3*), which range from 12.5 to 19.3 ng/L and average 16 ng/L.

Once the isotherm linearity limit had been established and the isotherm data within linear limits had been evaluated, sorption isotherms were found to be linear for all soils and f_s studied. Typical linear equilibrium sorption isotherms for soils 91 and 96 at a f_s of 0.5 are shown in Figure 3.

Cosolvent Theory. Isotherm data used to evaluate the cosolvent theory are summarized in Table IV. These include isotherm data reported in Tables II and III for a f_s of 0.5 and 1.0, respectively, as well as data from isotherm experiments conducted at a f_s of 0.25 and 0.75. K_D values in Table IV for soil 91 at a f_s of 0.5 and 1.0 reflect averages of all corresponding K_D values listed in Tables II and III, respectively. K_D values in Table IV for soil 96 at a f_s of 0.5 and 1.0 reflect averages of K_D values for 30 and 90 days of contact in Table II and 10–90 days of contact in Table III, respectively.

Most of the sorption data in Table IV are for $f_s \geq 0.5$. Experiments to evaluate sorption at a f_s of 0.25 yielded adequate statistical results only for soil 91. It was not possible to evaluate sorption of TCDD to soil 96 at a f_s of 0.25 or for either soil at lower f_s by the procedures utilized in this study due to detection limits for [^{14}C]TCDD, experimental difficulties in separating the soil and liquid phases, and possibly to nonattainment of equilibrium. The latter two factors appeared to contribute to complications in evaluating sorption to soil 96 at a f_s of 0.25, as was evident from a high degree of variability between data points in single isotherm experiments as well as between

Table IV. Summary of Sorption Isotherm Data Used To Evaluate Cosolvent Theory

		volume fraction solvent, f_s			
soil	parameter[a]	1.0	0.75	0.5	0.25
91	K_D, mL/g	0.60	3.2	120	1 800
	n[b]	(m = 4)	14	(m = 7)	15
	r^2		0.98		0.98
	s		0.007		0.04
	K_m, mol/g	0.015	0.11	5.0	88
	$K_{m,oc}$	2.2	16	750	13 000
	log $K_{m,oc}$	0.35	1.2	2.9	4.1
96	K_D, mL/g	11	68	1400	
	n[b]	(m = 3)	15	(m = 2)	
	r^2		0.99		
	s		0.033		
	K_m, mol/g	0.27	2.3	58	
	$K_{m,oc}$	3.5	30	750	
	log $K_{m,oc}$	0.55	1.5	2.9	

[a] Tabulated data includes K_D (mL/g) ($K_D = \sum C_e q_e / \sum C_e^2$), the number of points in the isotherm (n), the coefficient of determination ($r^2 = K_D \sum C_e q_e / \sum q_e^2$) and the standard error of the estimate ($s = [(\sum (q_e - K_D C_e)^2)/(n-1)]^{1/2}$). [b] Where a value of m is indicated, the tabulated K_D is the average of K_D values from m separate isotherm evaluations, each of which had $n > 9$.

Table V. Select Properties of Water/Methanol Mixtures

	volume fraction solvent, f_s				
property[a]	1.0	0.75	0.5	0.25	0.0
volume fraction methanol, f_s	1.00	0.75	0.50	0.25	0.00
mass fraction methanol, f_m	1.00	0.704	0.442	0.209	0.000
mole fraction methanol, f_{mol}	1.00	0.572	0.309	0.130	0.000
liquid density, p_{mix}, g/mL	0.792	0.872	0.927	0.965	0.998
molar volume, V, mL/mol	40.4	29.8	24.1	20.5	18.0

[a] Property values determined as follows: $f_s = V_m/(V_m + V_w)$, where V_i = volume of liquid i used to prepare mixture and m and w are methanol and water, respectively. $f_m = [1 + (p_w/p_m)(1 - f_s)/f_s]^{-1}$ where p_i = density of liquid i. $f_{mol} = [1 + (p_w M_m / p_m M_w)(1 - f_s)/f_s]^{-1}$ where M_i = molecular weight of liquid i. Values for p_{mix} are based on f_m and data for 20 °C in Table 3-111 of Perry and Chilton (*18*). $V = (1/p_{mix})[M_m f_{mol} + M_w(1 - f_{mol})]$.

replicate isotherms. Both factors contribute to negative bias in experimental determinations of K_D. On the basis of these observations for TCDD, caution must be excercised in utilizing K_D values for $f_s \leq 0.25$ in evaluating the cosolvent theory.

$K_{m,i}$ values in Table IV were determined by dividing $K_{D,i}$ by liquid-phase molar volume (V, mL/mol). Values of V were determined as shown in Table V. $K_{m,i}$ values were normalized on f_{oc} of the respective soils, giving values of $K_{m,i,oc}$ also listed in Table IV. Linear regression of the combined $K_{m,i,oc}$ data for both soils yields eq 4. $K_{m,i,oc}$ data

$$\log K_{m,i,oc} = -4.97 f_s + 5.30 \qquad r^2 = 0.98,\ s = 0.20 \quad (4)$$

and eq 4 are plotted in Figure 4. On the basis of the data for TCDD and these two soils, values of log $K_{m,i,oc}$ are well described by a single line over the entire range of f_s studied. These data show that the cosolvent theory applies to sorption of TCDD, as has been observed for sorption of other solutes to soils from water/methanol mixtures (*9*, *10*). The data of each soil collapse onto a single line when normalized on f_{oc}, as would be expected according to the cosolvent theory (*8*).

Extrapolated Estimate of Aqueous-Phase K_{oc}. The intercept value of 5.30 in eq 4 is equal to the logarithm of the aqueous-phase partition coefficient for TCDD ex-

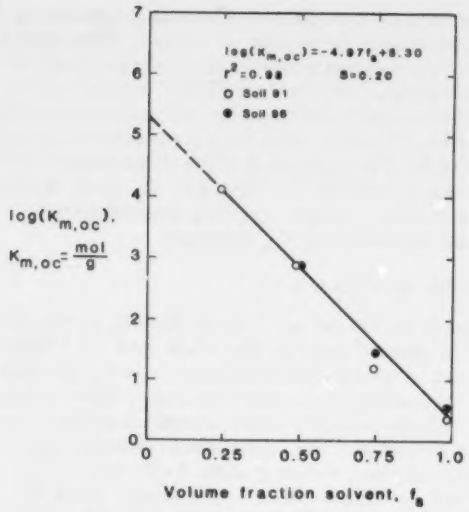

Figure 4. log–linear plot of sorption partition coefficients $K_{m,oc}$ versus f_s.

Table VI. Summary of α and σ_s Values for Water/Methanol Mixtures

solute	log K_{ow}	σ_s	$\alpha\sigma_s$	α	ref
naphthalene	3.35	3.79	1.90	0.53	10
naphthol	2.71	3.01	1.47	0.49	10
quinoline	2.04	2.86	1.34	0.47	10
3,5-dichloroaniline	2.59	2.96	1.69	0.57	10
anthracene	4.54[a]	5.6[b]	3.9[c]	0.70[c]	see footnotes
TCDD	6.64[d]	6.2	4.97	0.80	this study

[a] Karickhoff (*15*). [b] Based on solubility data presented by Nkedi-Kizza et al. (*9*) and Stephen and Stephen (*21*). [c] Values of $\alpha\sigma_s$ and α were calculated on the basis of data of Nkedi-Kizza et al. (*9*). [d] Marple et al. (*4*).

pressed in units of mol/g. This value can be converted to correspond to conventional dimensionless units by adding to it log V for water (log V = 1.26). The value of log K_{oc} (where K_{oc} is expressed in units of mL/g) for aqueous-phase sorption of TCDD to soils determined in this way, and the corresponding 95% confidence interval, is 6.6 ± 0.7. This value is in good agreement with the value of log K_{oc} of 6.7–7.0 predicted by using an average S for TCDD in water of 16 ng/L (*3*) and correlations of Chiou et al. (*19*) and Karickhoff et al. (*20*), respectively.

Significance of Slope $\alpha\sigma_s$. The slope of −4.97 of eq 4 corresponds to the term $-\alpha\sigma_s$ in eq 1. The value of $\alpha\sigma_s$ for TCDD is listed in Table VI along with the estimated value of σ_s (6.2) for TCDD in water/methanol systems and the apparent α (0.80) based on σ_s. The value of σ_s corresponds to the slope of the log–linear relationship between mole fraction solubility and f_s (*11*). This value was calculated by using solubilities of TCDD in solvent-free water and in methanol of 0.016 μg/L (*3*) and 10 mg/L (*1*), respectively (each was first converted to mole fraction), and by assuming log-linearity between S and f_s applies to TCDD in water/methanol mixtures (*11*). The apparent value of α was calculated by dividing $\alpha\sigma_s$ by σ_s.

Values of α and σ_s based on other reported studies of sorption of organic solutes to soils from water/methanol mixtures are also listed in Table VI. The data for naphthalene, naphthol, quinoline, and 3,5-dichloroaniline are reported by Fu and Luthy (*10*). The data for anthracene are based on K_D data presented by Nkedi-Kizza et al. (*9*). These latter K_D data were converted to mole-based K_m values and were normalized on f_{oc}. Regression analysis of

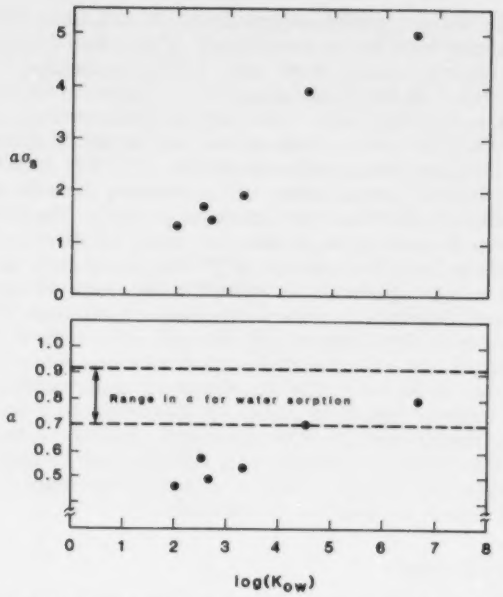

Figure 5. Variation in α and $\alpha\sigma_s$ versus log K_{ow} for sorption of organic solutes to soils from water/methanol mixtures.

log $K_{m,oc}$ versus f_s resulted in a value of $\alpha\sigma_s$ of 3.9. The value of α of 0.70 for anthracene is based on a σ_s of 5.6 determined from S of anthracene in water of 0.075 mg/L (*9*) and in methanol of 1.77% by weight (*21*).

The trends exhibited by $\alpha\sigma_s$ and α values listed in Table VI versus log K_{ow} are shown in Figure 5. log K_{ow} values are used to show the relative trend as hydrophobicity increases, rather than to imply that α and/or $\alpha\sigma_s$ should necessarily depend on log K_{ow}. The α values generally increase as log K_{ow} increases. For compounds with a log K_{ow} of 2.04–3.35, α was found to range from 0.47 to 0.57 (*10*). For anthracene (*9*), log K_{ow} is 4.54 and α was calculated to be 0.70. For TCDD, log K_{ow} is 6.64 (*4*) and α determined by the present study is 0.80. For comparison, a value of α of 0.7–0.92 has been suggested for sorption of a variety of organics to soil from water (*15*). This latter range in α is based on the data of condensed ring aromatics (α = 0.92) and an estimate of α in the range of 0.7–0.8 for highly chlorinated, high molecular weight compounds such as DDT or hexachlorobiphenyls (*15*). Karickhoff (*15*) suggests that the reduced α for the latter compounds derives from either kinetic or steric inhibition of sorption or decreased affinity of the solute for natural organic matter. It is of interest to note that as organic solute hydrophobicity increases, the value of α for sorption from water/methanol mixtures increases and approaches values of α corresponding to aqueous-phase sorption. The trend of observed $\alpha\sigma_s$ versus log K_{ow} shown in Figure 5 is similar to that for α in that $\alpha\sigma_s$ increases as organic solute hydrophobicity increases.

In interpreting their relatively low observed α values, Fu and Luthy (*10*) suggest that perhaps solvent–soil interactions were responsible for more effective sorption at high f_s. It was speculated that methanol expanded the soil organic matrix, resulting in increased accessibility of solute to the soil organic matter. Apparently, sorption of more hydrophobic compounds such as TCDD is not as significantly affected as is the sorption of less hydrophobic compounds. The variability in α versus log K_{ow} is presently under study.

Solvent–Soil Interactions. There was concern during the course of this study that soil-solvent interactions might

affect the results of these experiments in addition to effects expected from the cosolvent theory. The potential removal of organic matter from soils during contacting with methanol in the liquid phase was of particular concern. Numerous experiments were performed to investigate the effect of soil–solvent interactions on observed kinetic and equilibrium characteristics for sorption of TCDD, including the effect of precontacting and prewashing the soils with methanol prior to use in sorption experiments. The results of these experiments showed essentially no effect on the observed sorptive behavior of TCDD, particularly under the contacting procedures utilized in this study. However, visual observations made during these experiments of increases in liquid-phase turbidity and color suggest that material can be removed from soil over long contact periods (on the order of 90 days) and/or under conditions of rigorous agitation, either by extraction to generate dissolved materials or by scouring to generate colloidal matter. The manner in which this phenomena impacts sorption of organic solutes to soils in the presence of cosolvents is an issue for future study.

Conclusions

Sorption of ^{14}C-labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) to soils from water/methanol mixtures has been investigated by using batch shake testing. Six uncontaminated soils from the Times Beach, MO, area were utilized.

Sorption kinetics were influenced by the fraction of methanol in the liquid phase (f_s) and soil type. Sorption equilibrium at higher f_s was attained at shorter contact times. Sorption to the soil of highest organic carbon content (f_{oc}) required longer contact times to achieve sorption equilibrium than were required of the other soils studied. It is suspected that this reflects differences in the organic matter content of the high-f_{oc} soil relative to that of the other soils.

Linear equilibrium sorption isotherms have been observed for all soils and liquid systems studied. The liquid-phase concentrations above which isotherm data deviated from linearity support the aqueous solubility (S) of TCDD of 12.5–19.3 ng/L reported by Marple et al. (*3*).

Mole-based equilibrium sorption partition coefficients (K_m) were described by the cosolvent theory, which predicts a log–linear relationship between K_m and f_s. When normalized on f_{oc}, K_m values yielded $K_{m,oc}$ values, which were represented by a single log–linear relationship. Regression analysis of $K_{m,oc}$ data generated for f_s from 0.25 to 1.00 yields eq 4. From this relationship, the extrapolated estimate of log K_{oc} (where K_{oc} is the partition coefficient normalized on f_{oc}, mL/g) and associated 95% confidence interval for water-phase sorption is 6.6 ± 0.7. This value is in good agreement with the estimate of log K_{oc} of 6.7–7.0 for TCDD made by using an average value of S in water of 16 ng/L and regression equations relating log K_{oc} and log S.

The log–linear relationship of eq 4 suggests that the mobility of TCDD can be substantially increased in the presence of relatively high levels of miscible solvents in the liquid phase. However, this relationship predicts that methanol concentrations on the order of 1 g/L or lower would not significantly increase dioxin mobility over that expected in the absence of solvents in the liquid phase. While this conclusion applies to the sorption of TCDD in the presence of methanol, and presumably to sorption in the presence of other water-miscible solvents, it is presently unclear whether this conclusion can be extended to immiscible solvents.

The slope of the log–linear relationship between log $K_{m,oc}$ and f_s represents the product of α and σ_s. The latter is the slope of the log–linear relationship between mole fraction solubility and f_s, which for TCDD is estimated to be 6.2. The former term reflects solute–soil and solvent–soil interactions. For water sorption, α is expected to range from 0.70 to 0.92. For sorption of TCDD from water/methanol mixtures, a value for α of 0.80 was observed. Results of this and other studies suggest a general trend of α increasing as solute log K_{ow} increases.

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